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(54) WATER-BASE FLUOROPOLYMER DISPERSION

(57)Abstract:

PURPOSE: To obtain the subject dispersion which is very excellent in mechanical and chemical stabilities, has a high film-forming capability, and gives a coating film hardly water-permeable and excellent in resistances to weather and water.

CONSTITUTION: The objective dispersion is obt'd. by the emulsion polymn. of a copolymerizable monomer component at least contg. a fluoroolefin and a macromonomer having hydrophilic sites in the presence of a nonionic emulsifier having an HLB of 12-18.

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CLAIMS

[Claim(a)]

[Claim 1] Fluorine-containing polymer aqueous dispersion liquid obtained by carrying out the emulsion polymerization of a fluoro olefin and the copolymerizable monomer which makes an indispensable constituent the macro monomer which has a hydrophobic part under existence of the nonionic emulsifier of HLB 12-18.

[Claim 2] Fluorine-containing polymer aqueous dispersion liquid of claim 1 characterized by the nonionic emulsifier of HLB 12-18 not containing the poly fluoro alkyl group.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to fluorine-containing polymer aqueous dispersion liquid.

[0002]

[Description of the Prior Art] When the copolymer which consists of a fluoro olefin, cyclohexyl vinyl ether, and various kinds of monomers in addition to this is meltable to an organic solvent and is used as a coating at a room temperature, it is transparent, and has high gloss, giving the paint film moreover equipped with the outstanding properties which a fluororesin has, such as high weatherability, water and oil repellency, resistance to contamination, and non-adhesiveness, is known (for example, JP.55-44083A), and use is increasing in fields, such as construction.

[0003] Since regulation is being performed from a viewpoint of air pollution to use of an organic solvent on the other hand in recent years, the need over the water paint and powder coatings which do not use an organic solvent is increasing, the examination for it is made also about the fluororesin, and it is reported about the thing without a functional group that it can manufacture by the emulsion polymerization (JP.55-25411A).

[0004] Moreover, the method of obtaining the fluorine-containing copolymer which has hydroxyl according to an emulsion polymerization is indicated by JP.57-34107A and JP.61-231044A. However, by these approaches, when it made it indispensable to use together an emulsifier and a hydrophilic organic solvent and both an emulsifier, and both [hydrophilic / hydrophilic either or] were not used, even if aqueous dispersion liquid were not obtained or aqueous dispersion liquid were obtained, there was a problem that mechanical and chemical stability were bad and caused condensation and sedimentation during preservation extremely.

[0005] Furthermore, the aqueous dispersion liquid obtained by these approaches may be inferior in the resistance to contamination of the paint film from which film formation nature is bad, and is obtained.

[0006]

[Problem(s) to be Solved by the Invention] This invention tends to solve the trouble which the above-mentioned conventional technique has. Namely, it aims at offering newly the fluorine-containing polymer aqueous dispersion liquid the water resisting property of a paint film and whose resistance to contamination were excellent in film formation nature, and improved.

[0007]

[Means for Solving the Problem] This invention is made that the above-mentioned trouble should be solved, and tends to offer the fluorine-containing polymer aqueous dispersion liquid obtained by carrying out the emulsion polymerization of a fluoro olefin and the copolymerizable monomer which makes an indispensable constituent the macro monomer which has a hydrophilic part under existence of the nonionic emulsifier of HLB 12-18.

[0008] In this invention, a with a carbon numbers [such as vinylidene fluoride trifluoro ethylene, chlorotrifluoroethylene, tetrafluoroethylene, pentafluoropropylene, and hexafluoropropylene,] of about two to four fluoro olefin is preferably adopted as a fluoro olefin. Especially a par halo olefin is desirable.

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manufactured by the approach which Yamashita and others has stated to Polym.Bull. and 5,335 (1981). That is, by carrying out the radical polymerization of the ethylene nature partial saturation monomer which has a hydrophilic radical under existence of the initiator which has the functional group which can be condensed, and a chain transfer agent, manufacture the polymer which has the functional group which can be condensed, subsequently to the functional group of this polymer the compound like glycidyl vinyl ether and the glycidyl allyl compound ether is made to react, and the approach of introducing a radical polymerization nature partial saturation radical into an end etc. is illustrated.

[0018] As an ethylene nature partial saturation monomer used for manufacture of this macro monomer Acrylamide, methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, 2-methoxy ethyl acrylate, 2-methoxy ethyl methacrylate, diacetone acrylamide, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxy butyl acrylate, There are acrylic ester of hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxy butyl methacrylate, and polyhydric alcohol, methacrylic ester of polyhydric alcohol, vinyl pyrrolidone, etc.

[0019] In addition, there are acrylamide, the derivative and methacrylamide, its derivative, N-methylol acrylamide derivative, ethyl-acrylate carbonyl, a methyl-acrylate TORGU recall, 2-hydroxyethyl acryloyl phosphate, butoxy ethyl acrylate, etc. as a copolymerizable monomer.

[0020] Moreover, there are a - azobis-4-cyano valeric acid and 4 and 4 ' 2, 2'-azobis-2-amidinopropane hydrochloride, potassium persulfate, ammonium persulfate, azobisisobutyronitril, a benzoyl peroxide, etc. as an initiator used for manufacture of this macro monomer.

[0021] The fluorine-containing copolymer in this invention may include the unit containing the reactant radical chosen from hydroxyl, an epoxy group, a carboxylic-acid radical, a carbonyl group, and hydrazine residue besides the two above-mentioned sorts of units which carried out the polymerization.

[0022] Stability is not spoiled even if, as for the aqueous dispersion liquid of this invention, the fluorine-containing copolymer has the reactant radical. Moreover, when the fluorine-containing copolymer has the reactant radical, and it considers as the coating base, there is an advantage that the deck watertight luminaire which was extremely excellent with concomitant use of a curing agent, and the paint film which has solvent resistance can be obtained.

[0023] Moreover, there is the approach of copolymerizing a hydroxyl content monomer or a method of making the unit which is made to carry out the macromolecule reaction of the polymer, and contains hydroxyl form as introductory approach of the unit containing hydroxyl which carried out the polymerization. Here, as a hydroxyl content monomer, the hydroxyalkyl ester of the acrylic acid like the hydroxyalkyl vinyl ether like hydroxy butyl vinyl ether, the hydroxyalkyl allyl compound ether like the hydroxyethyl allyl compound ether, hydroxyethyl acrylate, and hydroxyethyl methacrylate or a methacrylic acid, hydroxyalkyl vinyl ester, hydroxyalkyl allyl ester, etc. are illustrated.

[0024] Moreover, after carrying out copolymerization of the vinyl ester in which the hydrolysis after a polymerization is possible as an approach of making the unit which is made carrying out the macromolecule reaction of the polymer, and contains hydroxyl forming, you make it hydrolyze and the approach of making hydroxyl form etc. is illustrated.

[0025] Moreover, there are the approach of copolymerizing a carboxylic-acid radical content monomer and the approach of making a dibasic-acid anhydride react to the polymer which has hydroxyl, and forming a carboxylic-acid radical as introductory approach of the unit containing a carboxylic-acid radical which carried out the polymerization.

[0026] Here, as a carboxylic-acid radical content monomer, it is CH₂=CHOR1OCOR2COOMCH₂=CHCH₂R3OCOR4COOM (R1 and R3 are the alkyl group of carbon numbers 2-15). R2 and R4 The shape of a straight chain, the annular hydrocarbon group of saturation or partial saturation, radical in which M contains hydrogen, alkali metal, or nitrogen, etc. — it is illustrated.

[0027] The unit containing an epoxy group which carried out the polymerization can be introduced by copolymerizing the monomer containing an epoxy group.

[0028] As a monomer containing an epoxy group, epoxy group content alkyl acrylate or methacrylate, such as epoxy group content alkyl allyl compound ether, such as epoxy group

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[0009] It is important that the fluorine-containing copolymer obtained according to an emulsion polymerization has the unit based on the macro monomer which has a hydrophilic part which carried out the polymerization in the fluorine-containing polymer aqueous dispersion liquid of this invention. Since this unit is included as an indispensable constituent of a fluorine-containing copolymer, mechanical and the chemical stability of aqueous dispersion liquid are not only improved, but film formation nature, the water resisting property of a paint film, etc. can improve.

[0010] The hydrophilic part of the macro monomer which has a hydrophilic part in this invention expresses the part which has a hydrophilic radical or the part which has association of a hydrophilic property, and the part which consists of such combination.

[0011] Although it may be any of ionicity, nonionicity, both sexes, and such combination, since this hydrophilic radical has [*****] a problem in the chemical stability of these fluorine-containing polymer aqueous dispersion liquid when the above-mentioned hydrophilic part consists only of a unit which has the hydrophilic radical of ionicity, it is desirable to combine with the part which combines with the part which has the hydrophilic radical of nonionicity or both sexes preferably, or has association of a hydrophilic property.

[0012] Moreover, a macro monomer means the polymer of the low molecular weight which has a radical polymerization nature partial saturation radical at the piece end, or the thing of oligomer. That is, it is the compound which has a radical polymerization nature partial saturation radical at the piece end, and has at least two repeat units. Although it changes with classes of repeat unit, 100 or less things are desirable from fields, such as polymerization nature and a water resisting property, and a repeat unit is usually adopted.

[0013] As a macro monomer which has a hydrophilic part, it is (1) CH₂=CHO(CH₂)_k[O(CH₂)_m]_nOX (k is the integer of 1-10), m is the integer of 1-4, n is the integer of 2-20, X is H or a low-grade alkyl group.

(2) CH₂=CHCH₂O(CH₂)_k[O(CH₂)_m]_nOX (k is the integer of 1-10), m is the integer of 1-4, n is the integer of 2-20, X is H or a low-grade alkyl group.

(3) CH₂=CHO(CH₂)_k[O(CH₂)_m]_nOX (k is the integer of 1-10), m is the integer of 1-4, n is the integer of 2-20, X is H or a low-grade alkyl group. The oxyethylene unit and the oxypropylene unit may be arranged with the block and which the random mold.

(4) CH₂=CHCH₂O(CH₂)_k[O(CH₂)_m]_nOX (k is the integer of 1-10), m is the integer of 1-4, n is the integer of 2-20, X is H or a low-grade alkyl group. The oxyethylene unit and the oxypropylene unit may be arranged with the block and which the random mold.

(5) CH₂=CHO(CH₂)_k[O(CH₂)_m]_nOX (k is the integer of 1-10), m is the integer of 1-4, n is the integer of 2-20, X is H or a low-grade alkyl group.

The polyester polyester which has a radical polymerization nature partial saturation radical at which piece end is illustrated. [BR] [0014] Especially, since that in which a piece end has the structure of a vinyl ether mold is excellent in copolymeric [with a fluoro olefin], it is adopted preferably. Since what especially a polyether chain part becomes from an oxyethylene unit, or an oxyethylene unit and an oxypropylene unit is excellent in the hydrophilic property etc., it is desirable.

[0015] Moreover, unless it has at least two oxyethylene units, many properties, such as stability, are not attained. Moreover, since that more than whose one half of an oxy-alkylene unit is an oxyethylene unit is excellent in especially a hydrophilic property and excellent in stability, it is desirable. Moreover, a water resisting property, weatherability, etc. of a paint film worsen, and what has the too much large number of oxy-alkylene units does not have them. [desirable]

[0016] Or the macro monomer which has this hydrophilic part carries out the polymerization of formaldehyde and the dol to the vinyl ether or the allyl compound ether which has hydroxyl, it can be manufactured by carrying out ring opening polymerization of the compound which has alkylene oxide or a lactone ring etc.

[0017] Moreover, the ethylene nature partial saturation monomer of a hydrophilic property may be a macro monomer which has the chain which carried out the radical polymerization and has a radical polymerization nature partial saturation radical like vinyl ether or the allyl compound ether at the end as a macro monomer which has a hydrophilic part. Such a macro monomer can be

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content alkyl vinyl ether, such as glycidyl vinyl ether, and the glycidyl allyl compound ether, glycidyl acrylate, and glycidyl methacrylate, etc. are illustrated.

[0029] Moreover, a carbonyl group can be introduced by copolymerizing a carbonyl group content monomer, and hydrazine residue is obtained by carrying out 0.02-1 molar-quantity combination per mol of carbonyl groups, and making dicarboxylic acid dihydrazide (for example, isophthalic acid dihydrazide, adipic-acid dihydrazide) and a hydrazine hydrate heat and react to a carbonyl group content polymer.

[0030] The unit based on a monomer with the as copolymerizable fluorine-containing copolymer in this invention as these other than the above-mentioned unit may be included. As this monomer, methacryloyl compounds, such as acryloyl compounds, such as allyl compounds, such as vinyl system compounds, such as aromatic series vinyl compounds, such as vinyl ester, such as vinyl ether, such as olefins, such as ethylene and a propylene, ethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, and cyclohexyl vinyl ether, and butanoic acid vinyl ester, octanoic-acid vinyl ester, styrene, and vinyltoluene, and the ethyl allyl compound ether, and butyl acrylate, and ethyl methacrylate, etc. are illustrated. Especially, olefins, vinyl ether, vinyl ester, allyl compound ether, and allyl ester are adopted preferably.

[0031] As olefins, a with a carbon number of about two to ten thing is desirable, and what has the alkyl group of the shape of the shape of a with a carbon number of about two to 15 straight chain, the letter of branching, or alkylic as vinyl ether, vinyl ester, allyl compound ether, and allyl ester is adopted preferably here.

[0032] A part of hydrogen [at least] which combined this monomer with carbon may be permuted by the fluorine.

[0033] As for the fluorine-containing copolymer in this invention, it is desirable that the part based on the macro monomer in which the unit based on a fluoro olefin which carried out the polymerization has a 20-80-mol % and hydrophilic-property part which carried out the polymerization is 0.1-25-mol % of a rate.

[0034] Since water-dispersion will get very bad if many [when there are too few units based on a fluoro olefin which carried out the polymerization / weatherability is not fully demonstrated and / too], it is not desirable. It is especially desirable that it is [30-70 mol %].

[0035] Moreover, since water-dispersion gets very bad, and the weatherability of a paint film and a water resisting property will worsen if many [too] if there are too few units based on the macro monomer which has a hydrophilic part which carried out the polymerization, it is not desirable. In order to make the effectiveness which was extremely excellent in especially film formation nature attain, it is desirable that this unit is included at 0.3-20 mol % of a rate.

[0036] Moreover, when the unit containing a reactant radical which carried out the polymerization is included, it is desirable that it is less than [25 mol %]. Since it may become a hard weak thing or a water resisting property may fall under the effect of residual hydroxyl when water-dispersion falls and a paint film is made to harden when the rate of this unit is too large, it is not desirable.

[0037] Moreover, when this unit contains that in which the unit based on the macro monomer which has a hydrophilic part which carried out the polymerization has hydroxyl, that unit is included in the count containing the unit and hydroxyl based on the macro monomer which has a hydrophilic part which carried out the polymerization of both units which carried out the polymerization. As for units other than the unit based on the macro monomer which has the unit based on the above-mentioned fluoro olefin which carried out the polymerization, and a hydrophilic part which carried out the polymerization, it is desirable that it is [0-70 mol %]. If there are too many these units, weatherability worsens and is not desirable.

[0038] In this invention, it is important that HLB performs an emulsion polymerization to the bottom of existence of the nonionic emulsifier of 12-18. When HLB shifts from this range, the stability at the time of an emulsion polymerization will become low, or the stability of the obtained dispersion liquid will fall. Moreover, in an anionic emulsifier, although the stability at the time of an emulsion polymerization is high, when mineral matter is added, it is easy to condense the obtained dispersion liquid, and when it considers as a paint film further, a water resisting property tends to fall by the high hydrophilic property. Especially desirable HLB is 14-18.

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[0039] Moreover, as a lipophilic group of a nonionic emulsifier, what does not contain the poly fluoro alkyl group is desirable from a viewpoint of formation of a precise paint film. Specifically, the block copolymer of an alkylphenol ethylene oxide addition product, a higher-alcohol ethylene oxide addition product, ethylene oxide, and propylene oxide etc. can be illustrated. Although the amount of the emulsifier used can be suitably changed according to conditions, per [which should usually carry out an emulsion polymerization / 0.1] monomer 100 weight section - 5 weight sections extent are adopted preferably.

[0040] Initiation of the emulsion polymerization in this invention is performed by addition of a polymerization initiator like initiation of the usual emulsion polymerization. As this polymerization initiator, although the usual radical initiator can be used a water-soluble initiator is adopted preferably. Specifically Persulfate, such as an ammonium persulfate salt. The redox initiator which consists of combination with reducing agents, such as a hydrogen peroxide or these and a sodium hydrogensulfate, and a sodium thiosulfate. The inorganic system initiator of the system which made still a small amount of iron to these, ferrous salt, silver sulfate, etc. five together. Or organic system initiators, such as a hydrochloride of dibasic-acid peroxides, such as disuccinic acid peroxide and *js* RUTARU acid peroxide, and an azobis isobutyl amine and azobisisobutyronitrile are illustrated.

[0041] Although the amount of the polymerization initiator used can be suitably changed according to a class, emulsion-polymerization conditions, etc., per (which should usually carry out an emulsion polymerization / 0.005) monomer 100 weight section - 0.5 weight sections extent are adopted preferably. Moreover, although these polymerization initiators may carry out package addition, division addition may be carried out if needed.

[0042] Moreover, pH regulator may be used in order to raise pH of an emulsification object. As this pH regulator, organic bases, such as inorganic bases, such as a sodium carbonate, potassium carbonate, orthophosphoric acid hydrogen sodium, a sodium thiosulfate, and sodium tetraborate, and triethylamine, triethanolamine, dimethylethanolamine, and diethyl ethanolamine, are illustrated.

[0043] the addition of pH regulator — usually — per [0.05] emulsion-polymerization medium 100 weight section - 2 weight sections extent — it is 0.1 - 2 weight section extent preferably. The one where pH is higher is the inclination for a rate of polymerization to become quick.

[0044] Moreover, although optimum temperature is suitably selected according to the class of polymerization initiator, 0-100 degrees C of emulsion-polymerization initiation temperature are usually adopted especially preferably about 10-90 degrees C. Moreover, reaction pressure is usually 2-50kg/cm² especially 1-100kg/cm², although it can select suitably. It is desirable to adopt extent.

[0045] Although package preparation of the additives, such as a monomer, water, an emulsifier, and an initiator, may be carried out as it is and they may carry out a polymerization in this manufacture approach, before adding a polymerization initiator, epistators, such as a homogenizer, may be made to use and front-emulsify in order to make the particle diameter of a particulate material small and to raise many physical properties, such as the stability of dispersion liquid, and gloss of a paint film, and the polymerization of the initiator may be added and carried out after that. Moreover, a monomer may be divided, or you may add continuously and monomer presentations may differ in that case.

[0048] Although the aqueous dispersion liquid of this invention can be used as a water paint even when they remain as it is, they may mix a coloring agent, a plasticizer, an ultraviolet ray absorber, a leveling agent, a HAJIKI inhibitor, a hide weld flash inhibitor, a curing agent, etc. if needed.

[0047] A color, an organic pigment, an inorganic pigment, etc. are illustrated as a coloring agent. The amount plasticizers of macromolecules, such as low-molecular-weight plasticizers, such as what is well-known as a plasticizer, for example, dioctyl phthalate etc., a vinyl polymerization object plasticizer, and a polyester plasticizer, etc. are mentioned.

[0048] As a curing agent, urea-resins, such as melamine resin, such as block isocyanates, such as for example, a hexamethylene isocyanate trimer, or an emulsification dispersing element of those, a methylation melamine, a methylol-ized melamine, and a BUCHIRORU-ized melamine, a

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methylation urea, and a butyl-ized urea, can be mentioned. Moreover, pH regulator may be added in order to raise the stability of aqueous dispersion liquid.

[0049]

[Example] Although an example is given to below and this invention is concretely explained to it, this invention is not limited at all by this example etc. In addition, especially, number of copies in the following examples shows the weight section, as long as there is no notice.

[0050] The ethyl vinyl ether of the presentation shown in Table 1 in the autoclave with the agitator made from stainless steel of 200ml of one to examples 1-4 and example of comparison 4 content volume (EVE), cyclohexyl vinyl ether (CHVE), hydroxy butyl vinyl ether (HBVE). Prepare the macro monomer (EDVE) which has a hydrophilic part, ion exchange water, an emulsifier, potassium carbonate (K_2CO_3), a sodium hydrogensulfate ($NaHSO_3$), and ammonium persulfate ($(NH_4)_2S_2O_8$), and it contains an ice. It is nitrogen gas 30 gms/cm^2 it pressurizes and desoxygenates the mixture before the reaction. The reaction is carried out in a nitrogen atmosphere, degassing twice, and removing dissolved air, chlorotrifluoroethylene (CTFE) or tetrafluoroethylene (TFE) was taught and the reaction was performed at 30 degrees C for 12 hours.

[0051] In addition, EOVE is a compound shown by the following formula, and number average molecular weight is about 500.

$$\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H} \quad [0052]$$

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		実測例					比較例				
		1	2	3	4	1	2	3	4		
TPE		38.0	38.0	38.0	30.9	38.0	38.0	38.0	38.0		
CTPE		22.1	22.1	10.5		22.1	22.1	22.1	22.1		
CHVE		17.5	4.5	5.5		4.5	4.5	4.5	4.5		
HDVE		4.5	4.5	4.5	9.7	4.5	4.5	4.5	4.5		
EOVE											
KPS		0.08	0.08	0.08	0.11	0.08	0.08	0.08	0.08		
K ₂ CO ₃		0.35	0.35	0.35	0.34	0.35	0.35	0.35	0.35		
NaHCO ₃		0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62		
メチルアルコール		66.1	66.1	66.1	76.4	66.1	66.1	66.1	66.1		
Cf, COMI,						0.00					
C, H ₂ , (C ₂ H ₅) ₂ AO, II	HLB10.8	1.32	1.32	1.32	1.32		1.32				
乳											
乳化剤											
水											
C, H ₂ , (C ₂ H ₅) ₂ AO											
重合時の温度 (°C)		0.98	0.83	0.85	0.82	0.55	5.76	2.47	3.33		
重合時の時間 (h)		0.30	70	150	90	3.00	3.00	2.47	2.00		
重合時の圧力 (ppm)		200	100	150	80	100以上	100以上	100以上	100以上		
重合時の速度 (ppm)											

化学式は、水と脂肪酸と等重量の10%塩化カルシウムを添加、30分攪拌したものを記載する。
化学式は、水と脂肪酸と等重量の10%塩化カルシウムを添加、5分攪拌したものを記載する。
化学式は、水と脂肪酸と等重量の10%塩化カルシウムを添加、30分攪拌したものを記載する。

[0053] Coating combination was performed using the aqueous dispersion-liquid 71 section obtained by the above, the film formation assistant 38 section, the thickener 0.3 section, the pigment 15.4 section, the dispersant 0.8 section, the deforming agent 0.8 section, and the pure-water 10.3 section. In addition, for Ca-12 (Chisso make) and a thickener, the LEO screw CR (product made from the Hoechst composition) and a pigment are [a film formation assistant / NOPUKO sparse 44-C (Sannopuko make) and the deforming agent of titanium oxide (Ishihara Sanryo CR- 97) and a dispersant] the FS antifoams 90 (Dow Corning make).

[0054] On the slate plate, these coatings were applied with the air spray so that it might become

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40 micrometers of desiccation thickness, and they were dried for one week at 20 degrees C, and the test piece was obtained. The result of having performed weatherability and a waterproof and permeable trial about this test piece was shown in Table 2. Weatherproof evaluation made O what the fall of x and gloss is seldom accepted in that to which gloss fell remarkably 1000 hours after the QUV trial. Moreover, waterproof evaluation judged by the blister of a paint film, or the existence of exfoliation, after being immersed in 60-degree C warm water for one week. Permeable evaluation is JIS. It carried out according to A6910 and the case of 0.5ml or less was made into O.

**REGIONS WITH
FOREST**

[0055]
[Table 2]

	被處理例					比較例			
	1	2	3	4		1	2	3	4
耐水性	○	○	○	○		○	○	○	○
耐油性	○	○	○	○		×	○	×	○
耐水性	○	○	○	○		×	×	×	×

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[0056]

[Effect of the Invention] While the aqueous dispersion liquid of this invention have extremely excellent mechanical stability and chemical stability, it has good film formation nature, and the obtained paint film has weatherability and a high water resisting property, and cannot penetrate water easily.

[0057] The aqueous dispersion liquid of this invention which has these outstanding properties are very useful as a weatherproof water paint raw material. Moreover, the water paint using the aqueous dispersion liquid of this invention does not have worries in problems, such as a solvent regulation, and can be applied to a broad application. For example, it is useful to paint of inorganic building materials for sheathing, such as glass, a metal, and cement, etc.

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WRITTEN AMENDMENT

[Procedure revision]

[Filing Date] October 28, Heisei 4

[Procedure amendment 1]

[Document to be Amended] Specification

[Item(s) to be Amended] 0013

[Method of Amendment] Modification

[Proposed Amendment]

[0013] as the macro monomer which has a hydrophilic part — for example

(1) $\text{CH}_2=\text{CHO}(\text{CH}_2)_m[\text{O}(\text{CH}_2)_n]\text{nOX}$

(k is the integer of 1–10.) m is the integer of 1–4. n is the integer of 2–20. X is H or a low-grade alkyl group.

(2) $\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2)_k[\text{O}(\text{CH}_2)_m]\text{nOX}$

(k is the integer of 1–10.) m is the integer of 1–4. n is the integer of 2–20. X is H or a low-grade alkyl group.

(3) $\text{CH}_2=\text{CHO}(\text{CH}_2)_k[\text{OCH}_2\text{CH}_2]_m[\text{OCH}_2\text{CH}(\text{CH}_3)]_n\text{OX}$

(k is the integer of 1–10.) m is the integer of 2–20. n is the integer of 0–20. X is H or a low-grade alkyl group. The oxyethylene unit and the oxypropylene unit may be arranged with the block and which the random mold.

(4) $\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2)_k[\text{OCH}_2\text{CH}_2]_m[\text{OCH}_2\text{CH}(\text{CH}_3)]_n\text{OX}$

(k is the integer of 1–10.) m is the integer of 2–20. n is the integer of 0–20. X is H or a low-grade alkyl group. The oxyethylene unit and the oxypropylene unit may be arranged with the block and which the random mold.

(5) $\text{CH}_2=\text{CHO}(\text{CH}_2)_n[\text{O}(\text{CO}(\text{CH}_2)_m\text{O})]_k\text{H}$

(n is the integer of 1–10.) m is the integer of 1–10. k is the integer of 1–30.

The polyether polyester which has a radical polymerization nature partial saturation radical at which piece end is illustrated.

[Procedure amendment 2]

[Document to be Amended] Specification

[Item(s) to be Amended] 0028

[Method of Amendment] Modification

[Proposed Amendment]

[0028] Here, it is a carboxylic-acid radical content monomer,

$\text{CH}_2=\text{CHOR1OCOR2COOM}$

$\text{CH}_2=\text{CHCH}_2\text{R3OCOR4COOM}$

(R1 and R3 are the alkyl group of carbon numbers 2–15.) R2 and R4 The shape of a straight chain, the annular hydrocarbon group of saturation or partial saturation, radical in which M contains hydrogen, alkali metal, or nitrogen, etc. — it is illustrated.

[Procedure amendment 3]

[Document to be Amended] Specification

[Item(s) to be Amended] 0044

[Method of Amendment] Modification

[Proposed Amendment]

[0044] Moreover, although optimum temperature is suitably selected according to the class of polymerization initiator, 0–100 degrees C of emulsion-polymerization initiation temperature are usually adopted especially preferably about 10–90 degrees C. Moreover, reaction pressure is usually 2–50kg/cm² especially 1–100kg/cm², although it can select suitably. It is desirable to adopt extent.

[Procedure amendment 4]

[Document to be Amended] Specification

[Item(s) to be Amended] 0050

[Method of Amendment] Modification

[Proposed Amendment]

[0050] Examples 1–4, the examples 1–4 of a comparison

The ethyl vinyl ether (EVE) of the presentation shown in Table 1, cyclohexyl vinyl ether (CHVE), hydroxy butyl vinyl ether (HBVE), the macro monomer (EOVE) that has a hydrophilic part, ion exchange water, an emulsifier, potassium carbonate (K₂CO₃), a sodium hydrosulfite (NaHSO₃), and ammonium persulfate (APS) are prepared into the autoclave with the agitator made from stainless steel of 200ml of content volume, and it cools on ice, and is nitrogen gas 3.5kg/cm² it pressurizes and deaerates so that it may become. After having deaerated to 10mmHg after repeating this pressurization degassing twice, and removing dissolved air, chlorotrifluoroethylene (CTFE) or tetrafluoroethylene (TFE) was taught and the reaction was performed at 30 degrees C for 12 hours.

[Procedure amendment 5]

[Document to be Amended] Specification

[Item(s) to be Amended] 0051

[Method of Amendment] Modification

[Proposed Amendment]

[0051] In addition, EOVE is a compound shown by the following formula, and number average molecular weight is about 500.

$\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$

[Translation done.]

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[Procedure amendment 1]

[Document to be Amended] Specification

[Item(s) to be Amended] Whole sentence

[Method of Amendment] Modification

[Proposed Amendment]

[Document Name] Specification

[Title of the Invention] Fluorine-containing polymer aqueous dispersion liquid

[Claim(s)]

[Claim 1] Fluorine-containing polymer aqueous dispersion liquid obtained by carrying out the emulsion polymerization of a fluoro olefin and the copolymerizable monomer which makes an indispensable constituent the macro monomer which has a hydrophilic part under existence of the nonionic emulsifier of HLB 12-18.

[Claim 2] Fluorine-containing polymer aqueous dispersion liquid according to claim 1 in which the nonionic emulsifier of HLB 12-18 does not contain the poly fluoro alkyl group.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to fluorine-containing polymer aqueous dispersion liquid.

[0002]

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[Description of the Prior Art] When the copolymer which consists of a fluoro olefin, cyclohexyl vinyl ether, and various kinds of monomers in addition to this is meltable to an organic solvent and is used as a coating at a room temperature, it is transparent, and has high gloss, giving the paint film moreover equipped with the outstanding properties such as a fluororesin has, such as high weatherability, water and oil repellency, resistance to contamination, and non-adhesiveness. is known (for example, JP55-44083A), and use is increasing in fields, such as construction.

[0003] Since regulation is being performed from a viewpoint of air pollution to use of an organic solvent on the other hand in recent years, the need over the water paint and powder coatings which do not use an organic solvent is increasing, the examination for it is made also about the fluororesin, and it is reported about the thing without a functional group that it can manufacture by the emulsion polymerization (JP55-25411A).

[0004] Moreover, the method of obtaining the fluorine-containing copolymer which has hydroxyl according to an emulsion polymerization is indicated by JP57-34107A and JP61-231044A. However, by these approaches, when it made it indispensable to use together an emulsifier and a hydrophilic organic solvent and both an emulsifier, and both [hydrophilic / hydrophilic either or] were not used, even if aqueous dispersion liquid were not obtained or aqueous dispersion liquid were obtained, there was a problem that mechanical and chemical stability were bad and caused condensation and sedimentation during preservation extremely.

[0005] Furthermore, the aqueous dispersion liquid obtained by these approaches may be inferior in the resistance to contamination of the paint film from which film formation nature is bad, and is obtained.

[0006]

[Problem(s) to be Solved by the Invention] This invention aims at offering newly the fluorine-containing polymer aqueous dispersion liquid the water resisting property of a paint film and whose resistance to contamination are going to solve the trouble which the above-mentioned conventional technique has, and were excellent in film formation nature, and improved.

[0007]

[Means for Solving the Problem] This invention is made that the above-mentioned trouble should be solved, and offers the fluorine-containing polymer aqueous dispersion liquid obtained by carrying out the emulsion polymerization of a fluoro olefin and the copolymerizable monomer which makes an indispensable constituent the macro monomer which has a hydrophilic part under existence of the nonionic emulsifier of HLB 12-18.

[0008] In this invention, a with a carbon numbers [such as vinylidene fluoride trifluoroethylene, chlorotrifluoroethylene, tetrafluoroethylene, pentafluoropropylene, and hexafluoropropylene,] of about two to four fluoro olefin is preferably adopted as a fluoro olefin. Especially a per halo olefin is desirable.

[0009] It is important that the fluorine-containing copolymer obtained according to an emulsion polymerization has the unit based on the macro monomer which has a hydrophilic part which carried out the polymerization in the fluorine-containing polymer aqueous dispersion liquid of this invention. Since this unit is included as an indispensable constituent of a fluorine-containing copolymer, mechanical and the chemical stability of aqueous dispersion liquid are not only improved, but film formation nature, the water resisting property of a paint film, etc. improve.

[0010] The hydrophilic part of the macro monomer which has a hydrophilic part in this invention expresses the part which has a hydrophilic radical or the part which has association of a hydrophilic property, and the part which consists of such combination.

[0011] Although it may be any of ionicity, nonionicity, both sexes, and such combination, since this hydrophilic radical has [*****] a problem in the chemical stability of these fluorine-containing polymer aqueous dispersion liquid when the above-mentioned hydrophilic part consists only of a unit which has the hydrophilic radical of ionicity, it is desirable to combine with the part which combines with the part which has the hydrophilic radical of nonionicity or both sexes preferably, or has association of a hydrophilic property.

[0012] Moreover, a macro monomer means the polymer of the low molecular weight which has a radical polymerization nature partial saturation radical at the piece end, or the thing of oligomer. That is, it is the compound which has a radical polymerization nature partial saturation radical at

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the piece end, and has at least two repeat units. Although it changes with classes of repeat unit, 100 or less things are desirable from fields, such as polymerization nature and a water resisting property, and a repeat unit is usually adopted.

[0013] As the macro monomer which has a hydrophilic part -- for example

(1) $\text{CH}_2=\text{CHO}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{X}$

(k is the integer of 1-10) m is the integer of 1-4, n is the integer of 2-20, X is a hydrogen atom or a low-grade alkyl group.

(2) $\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2)_k\text{O}(\text{CH}_2)_m\text{X}$

(k is the integer of 1-10) m is the integer of 1-4, n is the integer of 2-20, X is a hydrogen atom or a low-grade alkyl group.

(3) $\text{CH}_2=\text{CHO}(\text{CH}_2)_k(\text{OCH}_2\text{CH}_2)_a(\text{OCH}_2\text{CH}(\text{CH}_3))_b\text{X}$

(k is the integer of 1-10) a is the integer of 2-20, b is the integer of 0-20, X is a hydrogen atom or a low-grade alkyl group. The oxyethylene unit and the oxypropylene unit may be arranged with the block and which the random mold.

(4) $\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2)_k(\text{OCH}_2\text{CH}_2)_a(\text{OCH}_2\text{CH}(\text{CH}_3))_b\text{X}$

(k is the integer of 1-10) a is the integer of 2-20, b is the integer of 0-20, X is a hydrogen atom or a low-grade alkyl group. The oxyethylene unit and the oxypropylene unit may be arranged with the block and which the random mold.

(5) $\text{CH}_2=\text{CHO}(\text{CH}_2)_k\text{O}(\text{CO}(\text{CH}_2)_p\text{O})_q\text{H}$

(k is the integer of 1-10) p is the integer of 1-10, q is the integer of 1-30, etc. -- the polyether polyester which has a radical polymerization nature partial saturation radical at the piece end is illustrated.

[0014] Especially, since that in which a piece end has the structure of a vinyl ether mold is excellent in copolymerization [with a fluoro olefin], it is adopted preferably. Since what especially a polyether chain part becomes from an oxyethylene unit, or an oxyethylene unit and an oxypropylene unit is excellent in the hydrophilic property etc., it is desirable.

[0015] Moreover, unless it has at least two oxyethylene units, many properties, such as stability, are not attained. Moreover, since that more than whose one half of an oxy-alkylene unit is an oxyethylene unit is excellent in especially a hydrophilic property and excellent in stability, it is desirable. Moreover, a water resisting property, weatherability, etc. of a paint film worsen, and what has the too much large number of oxy-alkylene units does not have them. [desirable]

[0016] Or the macro monomer which has this hydrophilic part carries out the polymerization of formaldehyde or the diol to the vinyl ether or the alkyl compound ether which has hydroxyl, it can be manufactured by carrying out ring opening polymerization of the compound which has alkylene oxide and a lactone ring etc.

[0017] Moreover, as a macro monomer which has a hydrophilic part, the ethylene nature partial saturation monomer of a hydrophilic property may be a macro monomer which has the chain which carried out the radical polymerization and has a radical polymerization nature partial saturation radical like vinyl ether or the alkyl compound ether at the end. Such a macro monomer can be manufactured by the approach which Yamashita and others has stated to Polym.Bull. and 5.335 (1981). That is, by carrying out the radical polymerization of the ethylene nature partial saturation monomer which has a hydrophilic radical under existence of the initiator which has the functional group which can be condensed, and a chain transfer agent, manufacture the polymer which has the functional group which can be condensed, subsequently to the functional group of this polymer the compound like glycidyl vinyl ether and the glycidyl alkyl compound ether is made to react, and the approach of introducing a radical polymerization nature partial saturation radical into an end etc. is illustrated.

[0018] As an ethylene nature partial saturation monomer used for manufacture of this macro monomer Acrylamide, methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, 2-methoxy ethyl acrylate, 2-methoxy ethyl methacrylate, diacetone acrylamide, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, and the hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, acryic ester of polyhydric alcohol, methacrylic ester of polyhydric alcohol, vinyl pyrrolidone, etc.

[0019] In addition, there are phosphoric ester of acrylamide, the derivative and methacrylamide,

its derivative, N-methylol acrylamide derivative, diethylene-glycol-monoethyl-ether monoacrylate, triethylene glycol monomethyl ether monoacrylate, and 2-hydroxyethyl acrylate, butoxy ethyl acrylate, etc. as a copolymerizable monomer.

[0020] Moreover, there are a - azobis-4-cyano valeric acid, and 4 and 4 ' 2, 2'-azobis-2-amidinopropane hydrochloride, potassium persulfate, ammonium persulfate, azobisisobutyronitril, a benzoyl peroxide, etc. as an initiator used for manufacture of this macro monomer.

[0021] The fluorine-containing copolymer in this invention may include the unit containing the reactant radical chosen from hydroxyl, an epoxy group, a carboxylic-acid radical, a carbonyl group, and hydrazine residue besides the two above-mentioned sorts of units which carried out the polymerization.

[0022] Stability is not spoiled even if, as for the aqueous dispersion liquid of this invention, the fluorine-containing copolymer has the reactant radical. Moreover, when the fluorine-containing copolymer has the reactant radical, and it considers as the coating base, there is an advantage that the deck watertight luminaire which was extremely excellent with concomitant use of a curing agent, and the paint film which has solvent resistance can be obtained.

[0023] Moreover, there is the approach of copolymerizing a hydroxyl content monomer or a method of making the unit which is made to carry out the macromolecule reaction of the polymer, and contains hydroxyl form as introductory approach of the unit containing hydroxyl which carried out the polymerization. Here, as a hydroxyl content monomer, the hydroxyalkyl ester of the acrylic acid like the hydroxyalkyl vinyl ether like hydroxy butyl vinyl ether, the hydroxyalkyl alkyl compound ether like the hydroxyethyl alkyl compound ether, hydroxyethyl acrylate, and hydroxyethyl methacrylate or a methacrylic acid etc. is illustrated.

[0024] Moreover, after carrying out copolymerization of the vinyl ester in which the hydrolysis after a polymerization is possible as an approach of making the unit which is made carrying out the macromolecule reaction of the polymer, and contains hydroxyl forming, you make it hydrolyze and the approach of making hydroxyl form etc. is illustrated.

[0025] Moreover, there are the approach of copolymerizing a carboxylic-acid radical content monomer and the approach of making a dibasic-acid anhydride react to the polymer which has hydroxyl, and forming a carboxylic-acid radical as introductory approach of the unit containing a carboxylic-acid radical which carried out the polymerization.

[0026] Here, it is a carboxylic-acid radical content monomer,

$\text{CH}_2=\text{CHOR}(\text{COOR})_2\text{COOM}$

$\text{CH}_2=\text{CHCH}_2\text{OR}(\text{COOR})_2\text{COOM}$

(R1 and R3 are the alkylene group of carbon numbers 2-15) R2 and R4 The shape of a straight chain of saturation or partial saturation, hydrocarbon group of annular bivalence, radical in which M contains a hydrogen atom, alkali metal, or a nitrogen atom, etc. -- it is illustrated.

[0027] The unit containing an epoxy group which carried out the polymerization can be introduced by copolymerizing the monomer containing an epoxy group.

[0028] As a monomer containing an epoxy group, epoxy group content alkyl acrylate or methacrylate, such as epoxy group content alkyl alkyl compound ether, such as epoxy group content alkyl vinyl ether, such as glycidyl vinyl ether, and the glycidyl alkyl compound ether, glycidyl acrylate, and glycidyl methacrylate, etc. are illustrated.

[0029] Moreover, a carbonyl group can be introduced by copolymerizing a carbonyl group content monomer, and hydrazine residue is obtained by carrying out 0.02-1 mole-quantity combination, and making dicarboxylic acid dihydrazide (for example, isophthalic acid dihydrazide, adipic-acid dihydrazide) and a hydrazine hydrate heat and react to a carbonyl group content polymer to one mol of carbonyl groups.

[0030] The unit based on a monomer with the as copolymerizable fluorine-containing copolymer in this invention as these other than the above-mentioned unit may be included. As this monomer, methacryloyl compounds, such as acryloyl compounds, such as alkyl compounds, such as vinyl system compounds, such as aromatic series vinyl compounds, such as vinyl ester, such as vinyl ether, such as olefins, such as ethylene and a propylene, ethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, and cyclohexyl vinyl ether, and butanoic acid vinyl ester, octanoic acid vinyl ester, styrene, and vinyltoluene, and the alkyl alkyl compound ether, and butyl acrylate, and

